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- (54) Ultraviolet and infrared radiation absorbing glass
- (57) An utraviolet and infrared radiation absorbing jass having excellent ultraviolet radiation absorbing power and bronze or neutral gray lint which is suitably used as a window glass for verbicles of automobiles and also as a window glass for constructional materials is provided. The glass comprises, in % by weight: basic glass components comprising 56 to 80% SiQ₂ 0.6 5%

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Description

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FIELD OF THE INVENTION

The present invention relates to an ultraviolet and infrared radiation absorbing glass having a bronze or neutral gray tint.

BACKGROUND OF THE INVENTION

In order to meet the demand for protection of interior trim of automobiles against deterioration, which has been increasing with the recent trend to Juxury of the interior trim, and to reduce the load of air conditioning, a glass having ultraviolet and infrared radiation absorbing power has recently been proposed as window glass of automobiles.

For example, a green tinted glass containing a relatively large amount of Fe_2O_3 and having enhanced heat radiation absorbing power and ultraviolet radiation absorbing power is developed as window glass of automobiles. In the bronze or brown tinted glass, ultraviolet radiation absorbing power is enhanced by using Ce_2 and TO_2 at Fe_2 and relation absorbing glass having bronze int disclosed in JP-A-6-4074 (file term "JP-A**). As used herein means an "unexamined published Japanese patent application") comprises, in % by weight, as basic glass components, 89 to 74% SiO_2 , 0.1 to 3.0% A_2O_3 , 2 to 4.5% MgO_3 , 80 to 11% Ce_2 , 15.1 to 16% Re_2O_3 , and 0.5 to 3.0% Re_2O_3 , 10 to 4.% SiO_3 , 69 to 74% SiO_2 + Re_2O_3 , 11 to 15% Ce_2O + MgO_3 , and 12 to 17% Re_2O + Re_2O_3 , 11 to 15% Re_2O + Re_2O_3 , 11 to 15% Re_2O + Re_2O_3 , 11 to 15% Re_2O + Re_2O_3 , 12 to 4.5% Re_2O_3 , 10 to 4.5% Re_2O_3

Further, a colored ultraviolet radiation absorbing glass disclosed in JP-A-6-345482 is a glass having a brown that comprising, in % by weight, 65 to 75% SiQ₂, 0.1 to 5% $M_{\rm QQ}$, 1 to 6% MgQ, 5 to 15% CaQ, 10 to 15% Na_QQ, 0.0 to 5% $M_{\rm QQ}$, 0.5 to 1.0% SQ₃, 0.2 to 1.5% CeQ₂, 0 to 1.0% CeQ₃, 0 to 1.0% SQ₃, 0.2 to 1.5% CeQ₃, 0 to 1.0% SQ₃, 0.2 to 1.5% CeQ₃, wherein 3 to 15% of the total fron-oxide in terms of FeQQ₃ is FeQ.

The above-described conventional ultraviolat and in rared radiation absorbing glasses have an ultraviolat radiation absorbing power impared by uttraviolat radiation absorption due to $Fe_{Q,Q}$, $e_{Q,Q}$ and TQ_{Q} and interactions among them. However, in the glass having a bronze or neutral gray tint using coloration of Se, the $Fe_{Q,Q}$ content must be suppressed to a relatively small level in order to maintain pink coloration of Se. Accordingly, if has been impossible to exclive both bronze or neutral gray tint and high ultraviolat radiation absorbing power. That is, when the TQ_Q content is increased, the glass tands to be vellowsin, while, even if the $Ce_{Q,Q}$ content is increased, Se sometimes cannot be tully colored depending on the oxidation and reduction state of the glass so that the ultraviolat radiation absorbing power in an effectively increased.

SUMMARY OF THE INVENTION

The present invention has been made in the light of the above-described problems associated with the conventional techniques.

Accordingly, an object of the invention is to provide a bronze or neutral gray-linted ultraviolet and infrared radiation absorbing glass particularly having a high ultraviolet radiation.

The ultraviolet and infrared radiation absorbing glass according to the present invention comprises, in % by weight:

basic glass components comprising

65 to 80% SiO₂, 0 to 5% B₂O₃ 0 to 5% A₂O₃, 0 to 10% MgO, 5 to 15% CaO, 10 to 18% Na₂O, 0 to 5% K₂O, 5 to 15% MgO + CaO, and 10 to 20% Na₂O + K₂O, and

coloring components comprising

0.20 to 0.50% total iron oxide (T-Fe₂O₂) in terms of Fe₂O₃.

0 to 3.0% CeO_2 , 0.025 to 6.0% La_2O_3 , 0 to 2.0% TiO_2 , 0.0002 to 0.005% CeO_1 , 0.0002 to 0.005% Se_1 , 0 to 0.01% NiO_2 and 0 to 1.0% SnO_3

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wherein 5 to 25% of the T-Fe₂O₃ in terms of Fe₂O₃ is FeO.

It is preferred in the ultraviolet and infrared radiation absorbing glass according to the present invention that the GeO₂ content in the coloring components is 0.5 to 2.0%.

It is further preferred in the ultraviolet and infrared radiation absorbing glass according to the present invention that the CoO₂ content in the coloring components is 1.4 to 2.0% and the TiO₂ content in the coloring components is 0 to 1.5%.

It is still preferred that the CeO₂ content in the coloring components is 1.55 to 2.0% and the TiO₂ content is 0 to 1.0%. It is still further preferred that the La₂O₃ content in the coloring components is 0.05 to 1.5%.

The ultraviolet and infrared radiation absorbing glass according to the present invention preferably has optical characteristics that a visible light transmission as measured with the CIE standard illuminant A is 70% or more and a total solar energy transmission as measured in a wavelength region of 300 to 2,100 nm is less than 72%, when the glass has a thickness of 3 25 to 6 25 mm.

Further, the ultraviolet and infrared radiation absorbing glass according to the present invention preferably has optical characteristics that a dominant wavelength as measured with the CIE standard illuminant C is 572 to 580 nm, and a total ultraviolet transmission defined in ISO 9050 as measured in a wavelength region of 297.5 to 377.5 nm is leas than 12%, when the class has a thickness of 3,25 to 6,25 nm.

DETAILED DESCRIPTION OF THE INVENTION

The reasons for limitations of the glass composition of the ultraviolet and infrared radiation absorbing glass according to the present invention are explained below. Hereinafter, all percents are by weight.

SiO₂ is a main component forming a skeleton of glass. If the SiO₂ content is less than 65%, the glass has poor durability, and if it exceeds 60%, it is difficult to melt the composition.

While B_2O_3 is a component generally used for improvement of durability of glass or as melting aid, it also functions to enhance ultraviolet absorption. If the B_2O_3 exceeds 5.0%, exertion of the ultraviolet transmission decreasing effect is extended to the visible region, so that not only the tint tends to be yellowish, but also disadvantages occur in forming a glass due to votalitization of B_2O_3 and the like. Accordingly, the upper limit of the B_2O_3 content should be 5.0%.

AlpO3 serves to improve durability of glass. If the AlpO3 content exceeds 5%, it is difficult to melt the composition. A preferred AlpO3 content is from 0.1 to 2%.

MgO and CaO both serve to improve durability of glass and also to control liquidus temperature and a viscosity of glass composition when forming a glass. If the MgO content exceeds 10%, the liquidus temperature rises. If the CaO content is less than 5% or higher than 15%, the liquidus temperature rises. If the total content of MgO and CaO is less than 5%, durability of the resulting glass deteriorates. If the total content oxcoods 15%, the liquidus temperature rises.

 N_{3Q} and K_{sQ} 0 are used as glass melting accelerator. If the N_{8Q} 0 content is less than 10%, or if the total content of N_{8Q} 0 and K_{sQ} 0 is less than 10%, the effect of melting acceleration is poor. If the N_{8Q} 0 content exceed 18%, or if the total content of N_{8Q} 0 and K_{sQ} 0 exceeds 20%, the durability of glass is decreased. K_{sQ} 0 increases pink coloration of Se and, at the same time, enhances the ultraviolet radiation absorbing power. It is not preferable that the K_{sQ} 0 exceeds 10%0, because it is more expensive than N_{sQ} 0.

Iron oxida is present in glass in the form of Fe₂O₃ (Fe³⁺) and FeO (Fe²⁺). FeO is a component which serves to enhance infrared radiation absorbing power, and Fe₂O₃ is a component which serves to enhance ultraviolet radiation absorbing power together with GeO₃ and TiO₂.

If the amount of the total iron oxide (T-Fe₂O₃) is too small, the infrared radiation absorbing power and ultraviolet radiation absorbing power are low. If the amount thereof is too large, the visible light transmission is decreased. Therefore, the preferable amount of the total in oxide is 0.20 to 0.50%.

If the amount of FeO is too small, the infrared radiation absorbing power is decreased, and if it is too large, the visible light transmission is decreased. Therefore, the preferable amount of FeO is 5 to 25% of TFe₂O₃ in terms of

CeO₂ is a component which serves to enhance ultraviolet radiation absorbing power, and is present in glass in the form of Ce³⁺ or Ce³⁺. In particular, Ce³⁺ is effective in ultraviolet absorption because absorption in the visible light region is small. If the CeO₂ content is too large, the absorption in the short wavelength side of the visible light region

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is too large, and the glass becomes yellowish. Therefore, the CeO_2 content is 3.0% or less. In order to obtain a further desirable ultravioler radiation absorbing power, the CeO_2 is preferably used in an amount of 0.5 to 2.0%, more preferably 1.4 to 2.0%, and most preferably 1.55 to 2.0%.

TiO₂ is a component for enhancing the ultraviolet radiation absorbing power particularly by the interaction with FeO. If the TiO₂ content is too large, the glass tends to be yellow-linted. Therefore, the TiO₂ content is 2.0% or less, preferably 0 to 1.5%, and more preferably 0 to 1.0%.

CoO is a component for forming bronze or neutral gray tint by the coexistence with Se. If the CoO content is less than 0.002%, a desired tint cannot be obtained, and if its content exceeds 0.005%, the visible light transmission is decreased.

Se is a component for obtaining bronze or neutral gray tint due to pink coloration in combination with the complementary color of CoO. If the Se content is less than 0.0002%, a desired tint cannot be obtained, and if it exceeds 0.05%, the visble light transmission is decreased.

NiO is a component for obtaining neutral gray tint. If the NiO content is too large, the visible light transmission is decreased. Therefore, it should be used in an amount of 0.01% or less.

SnO₂ converts to Sn²⁺ at high temperature side, and to Sn⁴⁺ at low temperature side. Therefore, due to this change in the valency, SnO₂ functions as a reducing and fining agent in mething the glass. Further, in the glass containing Se and having bronze or noutral gray thit, SnO₂ has effects of accelerating pink colcatation of Se and also decreasing the uttraviolat transmission. If the SnO₂ content exceeds 1,0%, an undissolved matter tends to be formed. Therefore, the SnO₂ content is referably O.6% or less.

The glass having the above-described composition of the present invention may further contain at least one of ZnO, MnO, V₂Q₃ or MoQ₃ in the total amount of 0 to 1%, and 0 to 1% of S in terms of SO₃ so long as the object of the present invention is not impaired.

The present invention will now be described in more detail by reference to the following Examples. It should however be understood that the invention is not construed as being limited thereto. Unless otherwise indicated, all parts, percents, ratios, and the like are by weight.

EXAMPLES 1 TO 13

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In order to obtain a given glass composition, silica sand, dolornite, limestone, soda sah, potassium carbonate, borco noxide, sald cake, fuerfic oxide, filanium oxide, cerium oxide, postal toxide, sodium selentie, nickle oxide, lannus oxide, lanthanum oxide and a carbonaceous material as a reducing agent were appropriately mixed. In Example 11, a mixture containing CeO₂ and LeO₃, at a weight ratio of about 5.3 was used as a raw material of CeO₂ and LeO₃, at mixed the selection of the control of the cont

These raw materials were melted at 1,500°C for 4 hours in an electric furnace. The molten glass was cast on a statines steel plate and anneated to obtain a glass plate having a thickness of about 7 mm. This glass plate was polished so as to have a thickness of either 3.5, 4.0 °5 mm.

The optical characteristics of the sample thus obtained were measured. That is, a visible light transmission (YA) measured with the CIE standard lituminant A a total solar energy transmission (TG), an ultraviolar radiation transmission (TU) defined in ISO 9050, and a dominant wavelength (Dw) and an excitation purity (Pe) measured with the CIE standard illiminant C were obtained.

The results obtained in the Examples are shown in Table 1 below. Table 1 shows a concentration of each component

in the samples obtained and optical characteristic values of those samples. In Table 1, concentrations are all % by weight, provided that the ratio of FeQ (in terms of Fe₂O₂) to T-Fe₂O₃ (FeOT-Fe₂O₃) is shown not by the percentage, but by an arithmicial ratio.

TABLE 1

10		Puamala 1	Example 2	Evample 3	Example 4	Example 5	5
10				70.5	67.4	70.6	
	SiO ₂	70.5	70.4	70.5	67.4	70.6	
15	B ₂ O ₂	1.0		-		-	
	Al ₂ O ₃	1,40	1.40	1.60	1.34	1.40	
	MgO	3.80	3.80	3.80	3.14	3.29	
20	CaO	8.00	7.90	7.70	7.94	8.32	
	Na ₂ O	13.00	13.00	12.70	. 12.65	13.25	
	K ₂ O	0.70	0.70	0.68	0.96	1.00	
25	T-Fe ₂ O ₃	0.41	0.35	0.25	0.45	0.45	
	FeO	0.076	0.044	0.040	0.048	0.052	
30	FeO/T-Fe ₂ O ₃	0205	0.140	0.178	0.117	0.129	
	CeO ₂	0.48	0.91	1.10	1.01	1.00	
	La ₂ O ₃	0.29	0.55	0.66	5.05	0.60	
35	TiO ₂	0.39	0.96	1.00	0.10	0.10	
	CoO	0.0005	0.0030	0.0035	0.0020	0.0020	
40	Se	0.0008	0.0009	0.0007	0.0011	0.0011	
	NiO	-		-		· · ·	
	SnO ₂	-	- 9	-	-	5.	
45	Thickness (mm) 4	4 .	3.5	3.5	3.5	
	YA (%)	71.4	70.4	71.6	73.8	72.6	
50	TG (%)	62.1	69.9	71.2	70.2	68.5	
	Tuv (ISO) (%)	9.7	7.9	10.4	9.5	11.5	
	Dw (nm)	578	576	577	577	578	
55	Pe (%)	10.9	7.9	5.9	6.8	7.0	

TABLE 1 (Cont'd)

	Example 6	Example 7	Example 8	Example 9	Example 10
SiO2	70.3	70.6	70.1	69.8	69.6
B ₂ O ₂	<u> -</u> .	-	- '	-	-
Al ₂ O ₃	1.40	1.50	1.39	1.39	1.39
MgO	3.80	3.80	3.27	3.25	3.24
CaO	7.90	7.70	8.27	8.23	8.21
Na ₂ O ·	13.00	12.70	13.17	13.10	13.11
K ₂ O	0.70	0.68	0.99	0.99	1.00
T-Fe ₂ O ₃	0.3.0	0.23	0.45	0.45	0.45
FeO ,	0.046	0.037	0.051	0.047	0.046
FeO/T-Fe ₂ O3	0.170	0.179	0.126	0.117	0.113
CeO₂	1.50	1.00	1.40	1.70	1.70
La ₂ O ₃	0.90	0.60	0.80	1.00	1.00
TiO ₂	0.23	1.20	0.10	0.10	0.10
CoO	0.0015	0.0038	0.0020	0.002	0.0020
Se	0.0016	0.0005	0.0011	0.001	0.0011
NiO .		0.0010	· -	-	-
SnO ₂	-	-	-		0.32
Thickness (mm) 4	3.5	3.5	3.5	3.5
YA (%)	73.8	7.1.8	72.6	73.7	72.7 .
TG (%)	69.8	71.9	68.8	70.0	69.8
Tuv (ISO) (%)	9.3	11.4	10.1	8.8	8.4
Dw (nm)	578	572	577	577	578
Pe (%)	6.6	4.0	6.6	6.8	7.5

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TABLE 1 (Cont'd)

5 .			Example 11	Example 12	Example 13
		SiO ₂	69.7	68.6	70.8
		B ₂ O2		-	
10		Al ₂ O ₃	1.39	1.36	1.45
		MgO	3.27	3.32	3.80
15		CaO	8.21	8.09	7.80
		Na ₂ O	13.12	12.87	13.00
		K ₂ O	0.99	0.97	0.73
20		T-Fe ₂ O ₃	0.35	0.35	0.35
		Fe0	0.040	0.042	0.055
25		FeO/T-Fe ₂ O ₃	0.128	0.134	0.174
		CeO ₂	1.60	1.60	1.75
		La ₂ O ₃	0.96	2.80	0.09
30		TiO ₂	0.05	0.05	0.23
		CoO -	0.0010	0.0010	0.0011
35	,	Se	0.0009	0.0007	0.0012
		NiO		-	-
		SnO ₂	0.32	_ ·	ē -
10		Thickness (nm)	5	5	4
		YA (%)	71.1	73.1	72.9
<i>15</i>		TG (%)	66.4	66.9	66.6
		Tuv (ISO) (%)	6.4	6.8	8.9
		Dw (nm)	578	577	578
50		Pe (%)	9.8	7.9	7.3

As is apparent from the results shown in Table 1 above, the samples according to the Examples are the bronze or neutral gray tinted glass with a thickness of 3.25 to 8.25 mm has optical characteristics that a visible light transmission (YA) as measured with the OTE standard illuminant A is 70% or more, a dominant wavelength (Ow) as measured with the OTE standard illuminant C is 572 to 580 nm, a total solar energy transmission (TG) is less than 72%, and an ultraviolet transmission (Truy defined in ISO 9050 is less than 12%.

COMPARATIVE EXAMPLES 1 TO 3

Comparative Examples to the present invention are shown in Table 2. Those comparative glasses do not contain LagQ₃ which is an essential component of the present invention, and is therefore not within the scope of the present invention. Comparative Examples 1 to 3 are the glass corresponding to these of Examples 4, 9 and 11, respectively, which each do not contain La₂Q.

TABLE 2

		IMDLE 2	
	Comparative Example 1	Comparative Example 2	Comparative Example 3
SiO ₂	- 71.0	70.5	70.4
B ₂ O ₂			
Al ₂ O ₃	1.41	1.40	1.40
MgO	3.31	3.28	3.40
CaO	8.36	8.32	8.29
Na ₂ O	13.32	13.24	13.25
K ₂ O	1.01	1.00 .	1.00
T-Fe ₂ O ₃	0.47	0.45	0.35
FeO	0.048	0.047	0.040
FeO/T-Fe ₂ O ₃	0.113	0.117	0.128
CeO ₂ .	1.01	1.70	1.60
La ₂ O ₃			
TiO ₂	0.10	0,10	0.05
Se	0.0020	0.0020	0.0010
CoO	0.0011	0.0011	0.0009 -
NiO	-		
SnO ₂		* .	0.32
Thickness (nm)	.3.5	3.5	5
YA (%)	73.9	73.7	71.1
TG (%)	70.1	70.0	66.4
Tuv (%)	12.1	· 9.5	7,2
Dw (nm)	578	577	578
Pe (%)	6.9	6.8	9.8

As being apparent from Tables 1 to 2, the glasses obtained in the Examples have a decreased ultraviolet transmission as compared with that of the glasses obtained in the Comparative Examples. Thus, it can be seen that the ultraviolet and infrared radiation absorbing glass having bronze or neutral gray first could be obtained in the Examples.

In order to examine chemical durability of the glasses of Examples 4 and 9 and Comparative Examples 1 and 2, each of the glasses was placed in a constant temperature and humidity bath maintained under the condition of saturated atmosphere at 80°C for 200 hours. The glass was taken out of the bath and cooled. The reflectance of the cooled glass was obtermined. The difference of the reflectance before or after introducing into the bath was obtermined. According to this method, the reflectance is decreased when the glass underse is modified. Therefore, the modification of the glass can be conveniently evaluated based on the degree of decrease in the reflectance. The reflectance of each glass is shown in Eable 9 below.

TABLE 3

	Change of rofloctance (%)			
Example 4	-0.63			
Example 9	-0.81			
Comparative Example 1	-2,24			
Comparative Example 2	-1.50			

As is apparent from Table 3, the glass of the Examples has a decrease in reflectance smaller than that of the Comparative Examples so that the surface is difficult to be modified. Therefore, it can be seen that the glass of the

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Examples has a high chemical durability.

As described in detail above, the ultraviolet and infrared radiation absorbing glass according to the present invention makes it possible to produce a bronze or neutral gray tinted glass having excellent ultraviolet radiation absorbing power.

Further, in view of the facts that the ultraviolet and infrared radiation absorbing glass of the present invention has excellent ultraviolet radiation absorbing power and also has bronze or neutral gray tint, when the glass is used as a window glass for vehicles of automobiles and also as a window glass for constructional materials, it is effective in protection of interior materials inside a room against deterioration and fading.

Furthermore, according to the ultraviolet and infrared radiation absorbing glass of the present invention, CeO₂ and La₂O₂ can be added as an inexpensive raw material having a low degree of purification. Therefore, an ultraviolet and infrared radiation absorbing glass having excellent ultraviolet radiation absorbing power and chemical durability can be produced at low cost.

While the invention has been described in dotall and with reference to specific examines thereof, it will be apparent to one skilld in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

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20 1. An ultraviolet and infrared radiation absorbing glas's comprising, in % by weight:

basic glass components comprising

65 to 80% SiO₂, 0 to 5% B₂O₃, 0 to 10% MgO, 5 to 15% CaO, 10 to 16% Ma₂O, 0 to 5% K₂O, 5 to 15% MgO + CaO, and 10 to 16% Ma₂O,

coloring components comprising

 $\begin{array}{lll} 0.20 \ \text{to} \ 50\% \ \text{lotal iron oxide} \ (\text{T-Fe}_2O_3) \ \text{in terms of Fe}_2O_3 \\ 0.025 \ \text{to} \ 50\% \ \text{Lag}_0, \\ 0.025 \ \text{to} \ 50\% \ \text{Lag}_0, \\ 0.10 \ \text{2.0\% TiO}_2, \\ 0.0002 \ \text{to} \ 0.05\% \ \text{CoO}, \\ 0.0002 \ \text{to} \ 0.05\% \ \text{So}, \\ 0.0002 \ \text{to} \ 0.05\% \ \text{So}, \\ 0.10 \ \text{to} \ 0.01\% \ \text{NIO}, \ \text{and} \\ 0 \ \text{to} \ 1.0\% \ \text{SnO}_2 \end{array}$

- 45 wherein 5 to 25% of said T-Fe₂O₃ in terms of Fe₂O₃ is FeO:
 - The ultraviolet and infrared radiation absorbing glass as claimed in claim 1, wherein the CeO₂ content in the coloring
 components is 0.5 to 2.0%.
- The ultraviolet and infrared radiation absorbing glass as claimed in claim 1, wherein the CeO₂ content in the coloring
 components is 1.4 to 2.0%, and the TiO₂ content in the coloring components is 0 to 1.5%.
 - The ultraviolet and infrared radiation absorbing glass as claimed in claim 1, wherein the CeO₂ content in the coloring
 components is 1.55 to 2.0%, and the TiO₂ content in the coloring components is 0 to 1.0%.
 - The ultraviolet and infrared radiation absorbing glass as claimed in any of claims 1 to 4, wherein the La₂O₃ content
 in the coloring components is 0.05 to 1.5%.

- The ultraviolet and infrared radiation absorbing glass as claimed in any of claims 1 to 5, wherein said glass has a
 visible light transmission of 70% or more as measured with the CIE standard illuminant A, when said glass has a
 thickness of 3.25 to 6.25 mm.
- The ultraviolet and infrared radiation absorbing glass as claimed in any of claims 1 to 6, wherein said glass has a solar energy transmission of less than 72%, when said glass has a thickness of 3.25 to 6.25 mm.
- The ultraviolet and infrared radiation absorbing glass as claimed in any of claims 1 to 7, wherein said glass has a dominant wavelength of 572 to 580 nm as measured with the CIE standard filluminant C, when said glass has a thickness of 3.2 to 6.25 mm.
 - The ultraviolet and infrared radiation absorbing glass as claimed in any of claims 1 to 6, wherein said glass has an ultraviolet transmission defined in ISO 9050 of less than 12%, when said glass has a thickness of 3.25 to 6.25 mm

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European Pate

EUROPEAN SEARCH REPORT

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